

UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP012743

TITLE: In Situ STM/STS Investigation of Light Induced
Naphthacenequinone Molecules Conformation Transformations

DISTRIBUTION: Approved for public release, distribution unlimited
Availability: Hard copy only.

This paper is part of the following report:

TITLE: Nanostructures: Physics and Technology International Symposium
[6th] held in St. Petersburg, Russia on June 22-26, 1998 Proceedings

To order the complete compilation report, use: ADA406591

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP012712 thru ADP012852

UNCLASSIFIED

In situ STM/STS investigation of light induced naphthacenequinone molecules conformation transformations

V. I. Panov[†], S. I. Vasil'ev[†], A. I. Oreshkin[†], N. I. Koroteev[‡]
and S. A. Magnitskii[‡]

[†] Chair of Quantum Radiophysics, Moscow State University, 119899 Moscow, Russia

[‡] International Laser Center, Moscow State University, 119899 Moscow, Russia

Abstract. Light induced conformational transformations of the of naphthacenequinone (NQ) molecules ordered in LB films are observed by means of scanning tunneling microscopy (STM). The distinct peak in local density of electronic states is detected which is characteristic for the 2-dimensional character of conductivity. Additional subband of electronic states has been found for NQ molecules in form A and not found in form B. The constant height STM images of individual molecules in the form A demonstrate an additional fine structure that indicates the conformational transition of molecules from A to B form. This transition is connected with the transfer of the phenoxy group from one oxygen to another and probably leads to shutdown some of tunneling channels.

1 Introduction

Photochromic molecules attract considerable and permanent interest due to their capability for reversible changing of their absorption and fluorescent spectra under irradiation at different wavelengths. In view of the development of new generation of ultra-high density optical data storage based on the use of photochromic molecules it is important to reveal fundamental mechanisms that lead to modification photochromic molecules characteristics (especially organized in Langmuir-Blodgett (LB) films) under exposure to light. Properties of the photochromic molecules embedded either into polymeric matrices or other media (liquid crystals, solutions etc) essentially depend on their environment. Langmuir-Blodgett technique permits to produce photochromic molecular structures packed with ultra high density on the surface of a substrate. LB films are typical two-dimensional (single layer films) or three-dimensional (multilayer films) ordered assemblies. Evidently, one expect that photochromic molecules incorporated in highly ordered LB films should exhibit the behavior that is not typical for free molecules or solutions. However, very little is known about physics aspects of photochromic reactions in LB films.

For particular molecules photo isomeric changes can be observed by means of precise methods based on scanning probe microscopy (such as scanning tunnel microscopy/spectroscopy—STM/STS, scanning force microscopy—SFM etc.). These methods in principal allow one to study electronic properties [1,2] and topology of particular molecules and their variations, caused by external optical irradiation, on a substrate surface with atomic resolution.

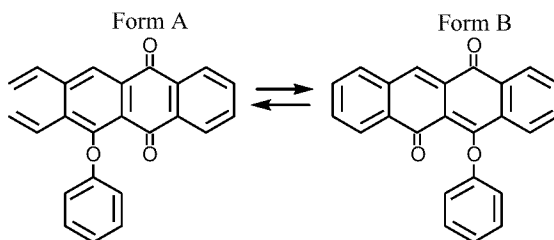


Fig 1. Schematic structure of two conformational forms (A and B) of 6-phenoxi-5, 12-naphthacenequinone molecules which occur during photocoloration ($A \rightarrow B$) and photobleaching ($B \rightarrow A$) reactions.

2 Experimental

To study the changes of electronic properties of NQ molecules and their possible conformational modifications during photochemical reactions we used STM and STS techniques. Molecules were deposited on a HOPG substrate using Langmuir-Sheffer technique to form different numbers of ordered molecular layers. Expected modification of naphthacenequinone molecular structure under transformation from para-form (form A) to ana-form (form B) is shown in Fig. 1. Variations of molecular properties in multilayer thin films caused by light irradiation may change the initial density distribution of electronic states, what be detected in STM and STS experiments.

In our experiments the photochemical reaction was initiated by light passed through interference filter with transmission maximum at 400 nm for the direct reaction ($A \rightarrow B$) and at 480 nm for the back reaction ($B \rightarrow A$). We used the incandescent lamp as a light source. After the interference filter radiation traveled through the wave-guide and than entered the tunnel gap of scanning tunneling microscope. Such a scheme has allowed to follow the changes of electronic properties of NQ molecules in processes of forward and reverse phototransitions by means of STM and STS methods.

LB film was transferred on the HOPG substrate under pressure of 5 mN/m. Average transfer coefficient $\langle k \rangle$ was equal to 0.84. We have found that LB films of naphthacenequinone molecules (1–40 monolayers) are capable to form the stable ordered structures on a surface of HOPG. The value of area occupied by each molecule is in the order of 2–2.3 nm² and is in a good agreement with the value of 2.7 nm² obtained from $\pi - S$ isotherm at the deposition pressure. Distance between molecular rows is in the range 0.58–0.6 nm and that between molecules in the row is 0.38–0.4 nm. Measurements of local density of electronic states of LB films have revealed a peak close to zero of bias voltage. In the approximation of a strong coupling it corresponds to the 2D character of differential conductivity of LB film and points to the existence of long-range interaction between molecules [3].

Another set of experiments have dealt with the investigation of LB film conductivity behavior during photoreactions. Substantial variation in the local density of electronic states for forward photoreaction has been observed for three-layer LB film. It is found that the form of the differential conductivity curve is significantly modified during photoisomerization. Upper graph depicted at Fig. 2 shows strong asymmetry of the curve for form A. There exist an additional contribution to at $U_t < 0$ in relation to form B,

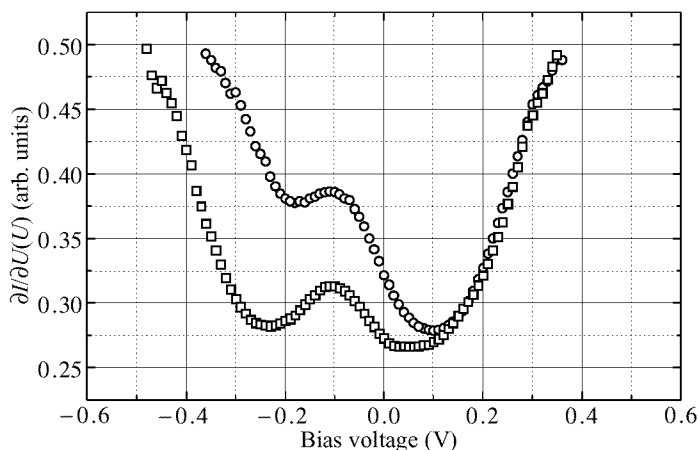


Fig 2. Dependence of differential conductivity of LB film on tunneling voltage (3 monolayers) before and after direct photoreaction. ○—A-form ; □—B-form.

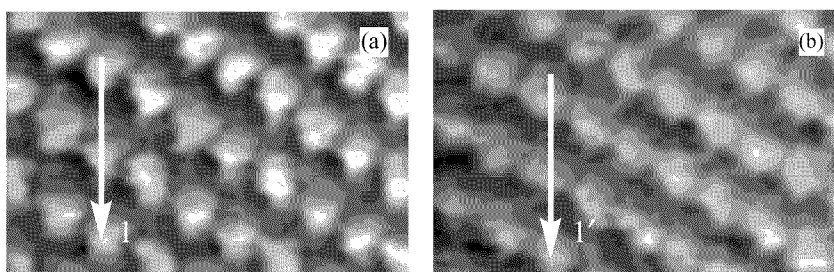


Fig 3. STM current images of the same portion of 3-layer naphthacenequinone LB films. a) form A, $I_t(x, y)$: $3.4 \text{ nm} \times 2.2 \text{ nm} \times 0.14 \text{ nA}$, b) form B, $I_t(x, y)$: $3.4 \text{ nm} \times 2.2 \text{ nm} \times 0.08 \text{ nA}$.

while the dependencies of LB film conductivity of A and B forms at $U_t > 0$ are rather similar. Such additive to the tunnel state density points to the origination of additional subband in the range of non filled electronic states of these LB films.

We have also studied the STM current images of individual molecules in NQ LB films. STM constant height images of 3-layer LB film corresponding to forms A and B of naphthacenequinone are presented in Fig. 3. Images (a) and (b) represent the selected site of the surface before and after direct photoreaction. Both pictures are registered under the same initial parameters: $U_t = -150 \text{ mV}$; $I_t = 0.4 \text{ nA}$. In these experiments we have found the spatial distinctions in STM current images of every molecule in LB layer for form A and B. These distinctions are clearly seen from Fig. 4 where current image sections of A and B forms of NQ molecules are depicted. The sections were get along the similar directions 1 and 1' (see Fig. 4) for the same molecules. As seen from Fig. 4, STM constant height image of 6-phenoxi-5,12-naphthacenequinone molecules in form A has $\sim 0.1 \text{ nA}$ amplitude, while the current amplitude for molecules in form B is $\sim 0.04 \text{ nA}$. Besides, the STM current image of molecules in form A possess an additional fine structure (see peak shifted to the edge of the molecular image). This

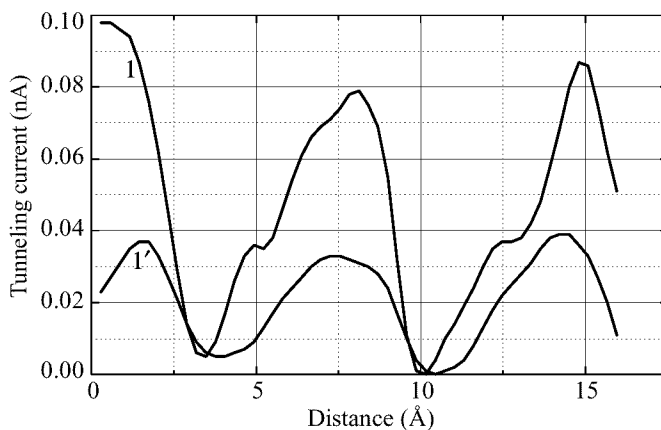


Fig 4. STM current image cross-sections according to arrows in Fig. 3. Curves 1, 1' correspond to directions 1, 1' at Fig. 3.

peculiarity is connected either with topological conformational transition of molecule or with the occurrence of additional tunneling channel after molecular conformation. To our opinion, the observed transition is due to oxygen bonding transfer that leads to occurrence of additional tunneling channel and, in ordered molecular system of LB film, to occurrence of additional subband.

3 Conclusion

We have demonstrated the direct observation of differential conductivity changes of NQ LB films under photochemical reaction by STM/STS methods. Unusual behavior of the differential conductivity of the molecular film probably corresponds to additional monotonous density of vacant states of the sample as a result of photoreaction and can be referred to conformational modification of naphthacenequinone molecules. The distinction in the STM constant height images of individual NQ molecules in different forms has been found that demonstrates the conformation transition during photoisomerization.

This work was financially supported by Memory Devices Inc. of the Constellation Group GmbH (Austria), partially by the Russian Ministry of Research (Nanostructures, grant 97-1086, Surface atomic Structures, grant 95-1.22) and the Russian Foundation of Basic Research (RFBR, grants 96-0219640a and 96-03-32867).

References

- [1] Supriyo Datta, Weidong Tian, Seunghum Hong, R. Reifenberger, Jason I. Henderson, Clifford P. Kubiak, *Phys. Rev. Lett.* **79** 2530–2533 (1997).
- [2] U. Düring, O. Zuger, B. Michel, L. Haussling, H. Ringsdorf, *Phys. Rev. B* **48** 1711 (1993).
- [3] N.S. Maslova, Yu.N. Moiseev, S.V. Savinov, R.G. Yusupov, *JETP Letters* **58** 524–528 (1993).